Chemical Kinetics: $k$ Models, Unimolecular/Termolec. Reactions

Jerry Seitzman

Collision Model: Example

$O_2 + Ar \rightarrow O + O + Ar$

- L-O-C Collision theory result

$$k = \frac{N}{\sigma} \sigma e^{-E_d/RT}$$

$$E_d = 494 \text{ kJ/mol}$$

$$k = P_{\text{steric}} \frac{6.02 \times 10^{23}}{\text{mol}} \left(16 \times 10^{-16} \text{ cm}^2\right) \sigma_{\text{elastic}} \frac{8 \cdot 1.38 \times 10^{-23} J/K \cdot T}{\pi (17.8 \cdot 1.673 \times 10^{-22} \text{ kg})} e^{\frac{59.500K}{T}}$$

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$k_{\text{coll}}/P_{\text{steric}}$</th>
<th>$k_{\text{exper}}$</th>
<th>$P_{\text{steric}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>800 K</td>
<td>$5.2 \times 10^{-19}$</td>
<td>$2.5 \times 10^{-17}$</td>
<td>0.02</td>
</tr>
<tr>
<td>1600 K</td>
<td>$9.9 \times 10^{-3}$</td>
<td>$1.7 \times 10^{-1}$</td>
<td>0.06</td>
</tr>
<tr>
<td>3200 K</td>
<td>$1.6 \times 10^{6}$</td>
<td>$9.7 \times 10^{5}$</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Collision Model
- Breaks down for low $T$
- Good for high $E_d$

$k$, cm$^3$/mole sec
Collision Model: Accuracy

- Collision model “works” for bimolecular reactions of simple molecules (atom + radical, simple dissoc.)
  - $P_{\text{steric}} \approx O(0.1)$
  - no extra energy barrier
- More complex molecules
  - $P_{\text{steric}}$ decreases
  - added energy barrier
  - need reduced $E_a$ barrier (only included transl. energy)

Potential Surfaces for Reactions

- Need to account for forces between multiple nuclei as they rearrange themselves during “collision”
- Can be modeled on computer with classical or quantum trajectories
- But difficult

$O + H_2 \rightarrow OH + H$
Activated Complex/Transition State

- Find minimum energy configuration of intermediate state
  - saddle point of energy surface
- Transition state highly unstable, but may exist for very small time
  - allows nuclei/electrons time to rearrange
- Use statistical mechanics to find $k$

Transition State Theory for $k$

- Assume unique minimum energy pathway exists (reaction coord.)
- Assume $AB$, $C$ and $ABC^*$ in equilibrium
  - from statistical mechanics
    $$\frac{N_{ABC^*}}{N_{AB}N_C} = \frac{Q_{ABC^*}}{Q_{AB}Q_C} e^{-E_{of}/RT}$$
    $$N_{ABC^*} = N_{AB}N_C \sqrt{\frac{2\pi mk_{\text{Boltz}}}{h}} \delta \frac{Q'_{ABC^*}}{Q_{AB}Q_C} e^{-E_{of}/RT}$$
    transl. degree of freedom of $ABC^*$ along $r$
TST Model – Production Rate

- Rate at which activated complexes become products (A+BC) depends on
  - number of activated complexes $N_{ABC^*}$
  - rate at which they move along $r$
    \[
    \frac{dN_{prod}}{dt} = N_{AB}N_{C} \sqrt{\frac{2k_{B}T}{\pi \mu}} \sqrt{\frac{2\pi \mu k_{B}T}{h}} \frac{Q'_{ABC^*}}{Q_{AB}Q_{C}} e^{-\frac{E_{af}}{RT}}
    \]

TST Model for $k$ – Result

- Converting to molar concentrations
  \[
  \frac{d[BC]}{dt} = \left[ AB \right] \left[ C \right] N_{Av} \frac{k_{Boltz}T}{h} \frac{q'_{ABC^*}}{q_{AB}q_{C}} e^{-\frac{E_{af}}{RT}}
  \]

\[
  k(T) = \kappa \frac{RT}{h} \frac{q'_{ABC^*}}{q_{AB}q_{C}} e^{-\frac{E_{af}}{RT}}
\]

- Find partition functions $q(T)$ from statistical mechanics
- Gives better $T$ dep., closer agreement to exper.

Other improvements
- Variational TST
  - if motion along $r$ is somehow hampered

AE/ME 6766 Combustion
Unimolecular Reactions

- Revisit unimolecular reactions $CO_2 \rightarrow CO + O$
  - experimental evidence indicates CO production can be 1st order (but not at low p)
  - how does this really happen
    - if collided with another molecule, 2nd order?
    - if collided with wall at same T as gas – how does energy of molecule increase to dissociation energy?
- Important to understand
  - important in first steps of some combustion systems

Lindemann-Hinshelwood Mechanism

$A \rightarrow \text{products}$

- Observed behavior is not due to single reaction
  - multistep reaction mechanism
  - excitation $A + M \rightarrow A^* + M$
    - activated complex with “long” lifetime
  - de-excitation $A^* + M \rightarrow A + M$
    - for $CO_2 \rightarrow CO + O$
    - $CO_2^*$ could be vibrationally excited state
  - unimolecular product formation $A^* \rightarrow \text{products}$
    - $\frac{d[\text{prod}]}{dt} = k_{\text{uni}}[A^*]$
    - but what is $[A^*]$?

AE/ME 6766 Combustion
Overall Production Rate

\[ A + M \rightarrow A^* + M \]

- Combine all steps to find \( \frac{d[A^*]}{dt} \)
\[
\frac{d[A^*]}{dt} = k_e [A][M] - k_{de} [A^*][M] - k_{uni} [A^*] \quad A^* \rightarrow \text{products}
\]

- Assume that \([A^*]\) is in **steady-state**
  - this assumption often made for minor species to simplify kinetics problems since \([\text{minor}] < [\text{major}]\) often means \(d[\text{minor}]/dt << d[\text{major}]/dt\)

\[
[A^*] = \frac{k_e [A][M]}{k_{de} [M] + k_{uni}}
\]

Unimolecular \( k \)

- Combining steady-state result into \( d[\text{prod}]/dt \)
\[
\frac{d[\text{prod}]}{dt} = k_{uni} [A^*] = k_{uni} \frac{k_e [A][M]}{k_{de} [M] + k_{uni}}
\]

- Apparent reaction rate constant
\[
A \rightarrow \text{products} \quad k^1 = k_{uni} \frac{k_e [M]}{k_{de} [M] + k_{uni}}
\]

\[
\frac{d[\text{prod}]}{dt} = k^1 [A] = \frac{k_e [M]}{1 + k_{de} [M]/k_{uni}}
\]
**Termolecular Reactions**

- Common three body collision: **recombination**
  \[ A + A + M \rightarrow A_2 + M \]
  - requires three molecules in the same place at “nearly” the same time
  - third body removes excess kinetic energy/velocity

- **Optional multistep mechanism**
  - “short” but finite lifetime of intermediate state (complex formation)
    \[
    \begin{align*}
    A + M &\rightarrow AM^* \\
    A + A &\rightarrow A_2^* \\
    A + AM^* &\rightarrow A_2 + M \\
    A_2^* + M &\rightarrow A_2 + M \\
    AM^* &\rightarrow A + M \\
    A_2^* &\rightarrow A + A
    \end{align*}
    \]